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Stability constants for the chloride complexes of palladium (II)

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STABILITY CONSTANTS FOR THE CHLORIDE COMPLEXES
OF PALLADIUM (II)

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NAVAL POSTGRADUATE SCHOOL
Monterey, California

THESIS

STABILITY CONSTANTS FOR THE CHLORIDE

COMPLEXES OF PALLADIUM (II)

by

Richard Leon Burke

Thesis Advisor: R. A. Reinhardt

December 1972

Stability Constants for the Chloride

Complexes of Palladium (II)

by

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Submitted in partial fulfillment of the
requirements for the degree of
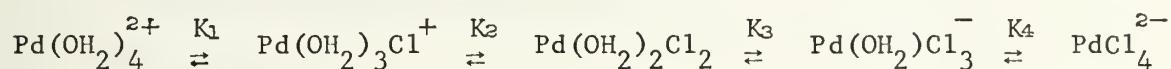

MASTER OF SCIENCE IN CHEMISTRY

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December 1972

ABSTRACT

Using absorbance data from Pd (II) solutions containing varying amounts of chloride ion, the stepwise formation constants were determined for the following system:

$$Pd(OH_2)_4^{2+} \; \overset{K_1}{\rightleftarrows} \; Pd(OH_2)_3Cl^+ \; \overset{K_2}{\rightleftarrows} \; Pd(OH_2)_2Cl_2 \; \overset{K_3}{\rightleftarrows} \; Pd(OH_2)Cl_3^- \; \overset{K_4}{\rightleftarrows} \; PdCl_4^{2-}$$

The values for K_1 and K_4 were obtained by curve fitting methods. K_2 and K_3 were found by regression and required statistical adjustment.

Anomalies arising from the resulting values and values obtained by other workers were discussed. Suggestions for further work in the chloro-Pd (II) system were made.

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ACKNOWLEDGEMENT

I. INTRODUCTION

A. GENERAL

As is the case with nickel (Ni), the +2 state of palladium (Pd) is
the more common state, although palladium (IV) is also important [Ref. 1].
Palladium in the +2 state was studied during this research. Along with
some of the other platinum group metals {Pt (II), Rh (I), Ir (I)},
Pd (II) has a d^8 electronic configuration and a coordination number of
four, such that the complexes formed are square planar [Ref. 2]. These
square-planar complexes are formed when a total of four neutral (e.g.,
NH_3, H_2O) or anionic (e.g., CN^-, CH_3^-, halide) ligands are tightly held
to the central metal cation by electron pair sharing, so-called dative
or coordinate bonding [Ref. 1]. Square planar is the geometric descrip-
tion of the complex, be it anionic, neutral, or cationic [Ref. 3]. The
square-planar complexes studied in this thesis research were:

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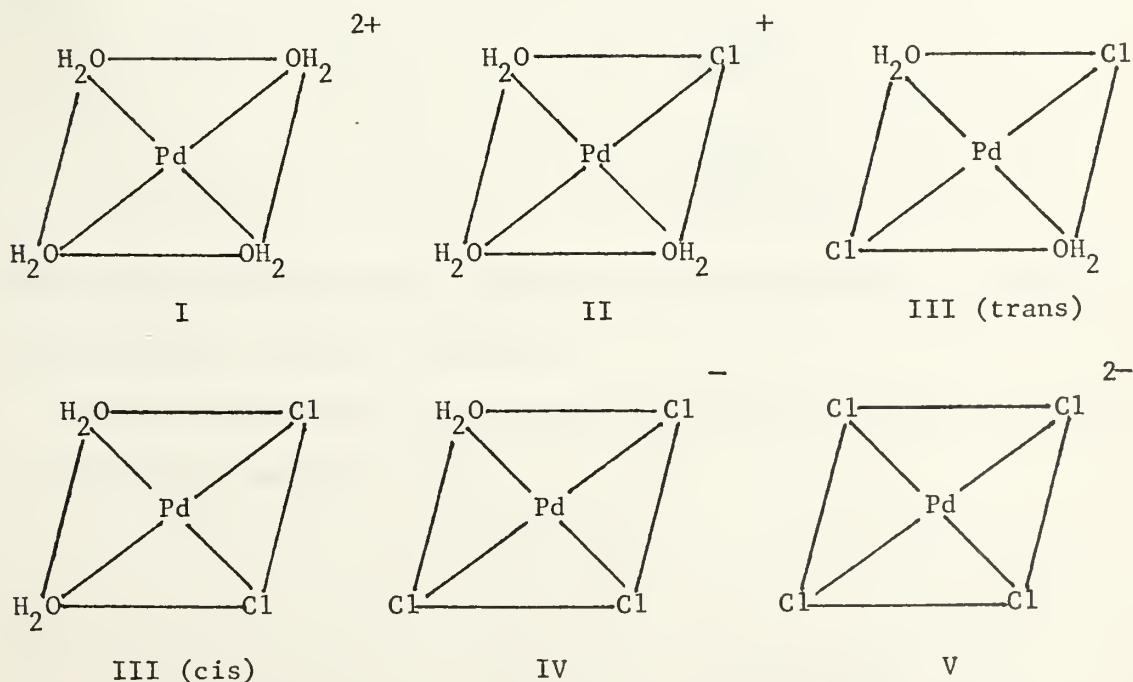
The currently accepted mechanism for substitution of square-planar complexes is believed to be essentially S_N2 with the formation of a trigonal bipyramid intermediate [Ref. 4]. However, of more importance to a study of equilibria in solutions is a distinction between reactivity and stability of complex ions in these solutions. The reactivity of a species refers to the speed with which transformations leading to the attainment of equilibrium will occur. The thermodynamic stability of a species is a measure of the extent to which a species will form from or be transformed into another species under certain conditions when the system has reached equilibrium [Ref. 1]. For example, if M is a transition metal, and L a monodentate ligand, then for the reaction
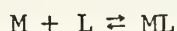
$$M + L \rightleftarrows ML$$

the thermodynamic equilibrium expression is

$$K_1 = \frac{[ML]}{[M][L]}$$

Similarly, if more ligands are bound to the metal by stepwise formation, then

$$ML + L \rightleftarrows ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_{n-1} + L \rightleftarrows ML_n \qquad K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \qquad [Ref. 5].$$
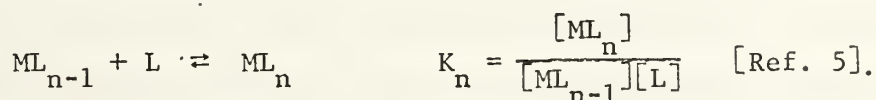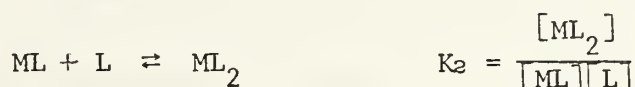
The subject of this thesis research is the determination of stepwise thermodynamic formation constants.

Another useful way of expressing equilibrium relations is by overall formation constants, e.g.,

$$\beta_1 = K_1$$

$$\beta_2 = K_1 K_2$$

$$\beta_n = K_1 K_2 \ldots K_n \quad [Ref. 6] .$$

As will be shown later in the treatment of data and results section, the K_i's for this research were determined by first obtaining the β_i's.

B. ABSORBANCE

Whether an equilibrium constant is explicitly expressed as a quotient of product and reactant concentrations or as a ratio of the forward and reverse rate constants [Ref. 7], the equilibrium constant remains a mathematical function of concentrations. The task then becomes to measure either the concentrations of the various species present in the system at equilibrium or another property which is linearly dependent on concentration, if the equilibrium constant is to be determined. According to Beer's Law, absorbance of a chemical species in solution is a property which is linearly dependent on concentration [Ref. 8]:

$$A = \epsilon c \ell$$

where, $A = \log_{10} I/I_0$
ℓ = optical path length through the sample (cm)
c = concentration of the absorbing species (moles/liter)
ϵ = proportionality constant called molar absorptivity when ℓ, c and A are defined as above.

Absorbance is an additive property -- that is to say it applies to a solution containing more than one absorbing species [Ref. 9], such as a solution containing more than one of the square-planar complexes studied in this research. For these reasons, absorbance has long been used as an analytical method and is used in this research in lieu of concentrations for determining equilibrium constants.

C. CHLORO COMPLEXES OF PALLADIUM (II)

During the time from the mid 1950's to present, a great deal of interest has been generated in the equilibria involving the various chloro complexes of palladium (II). Droll [Ref. 10] reported equilibrium

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constants of log K_1 = 6.1, log K_2 = 4.6, log K_3 = 2.4, and log K_4 = 2.6

for successive formation of chloride complexes of Pd (II). Rasmussen

and Jørgensen [Ref. 11] argued, however, that these values were high.

In addition, Rasmussen and Jørgensen list values reported by Weed [Ref.

12] of 4.4, 3.34, 2.34, and 1.38; by Burger [Ref. 13] of 3.88, 3.06,

2.14, and 1.34; and by Shchukarev et al [Ref. 14] of 4.34, 3.54, 2.61,

and 1.68. In light of the differences among the reported values, this

research was conducted as a part of a program concerned also with the

substitution kinetics in the system.

II. EXPERIMENTAL

A. MATERIALS

All materials in this research were reagent grade and were used without further purification.

A stock solution of tetraaquopalladium (II) ion was prepared by dissolving hydrated palladium (II) sulfate ($PdSO_4 \cdot xH_2O$) in 1M $HClO_4$ (Baker's analyzed reagent). The $PdSO_4$ was prepared by the method of Berzelius (1828) as reported by Mellor [Ref. 15]. Palladous nitrate (Fisher Scientific Company) was boiled in concentrated sulfuric acid (Baker analyzed reagent) for approximately 18 hours, adding H_2SO_4 when necessary. The resulting $PdSO_4$ was a mixture of the brick-red anhydrous and the brown, partly hydrated forms [Ref. 11]. When placed in 1M $HClO_4$, the brick-red anhydrous form would not dissolve, even after stirring with a magnetic stirrer for several days. The undissolved particles were filtered from the bright yellow solution. An absorbance spectrum was obtained in the visible range (350nm to 550nm) which indicated an absorbance maximum at $\lambda = 384$nm. The shape of the curve and the absorbance maximum agree very closely with that reported for $Pd(OH_2)_4^{2+}$ by Rasmussen and Jørgensen [Ref. 11] and by DeBerry [Ref. 16]. This indicated no inner-sphere sulfate complexes had formed.

A stock solution of tetrachloropalladate ion was prepared by dissolving 7.3545 grams of sodium tetrachloropalladate (Alfa Inorganics) in 500ml of solution using 0.1M HCl (CHEMTAM, 1/10 N, from BIO·RAD Laboratories) as solvent. The absorbance spectrum of this solution agreed with the absorbance data for $PdCl_4^{2-}$ from Cohen and Davidson [Ref. 17].

All solutions used in determining the equilibrium constants were prepared by dilutions of the stock solutions described above. Chloride ion concentration was varied by the addition of sodium chloride (Baker's analyzed reagent). Unit ionic strength was maintained in all solutions by addition of perchloric acid since the perchlorate ion has little or no tendency to form complexes [Ref. 4].

Tables I and II list the solutions prepared from the tetraaquo-palladium (II) stock and the tetrachloropalladate stock respectively.

B. ANALYSES

Both of the stock solutions previously described were analyzed for palladium content by precipitating the palladium out as a complex with dimethylglyoxime using the method outlined in Treadwell and Hall [Ref. 18]. To a three or four ml sample of stock solution was added approximately 12 ml of 1% dimethylglyoxime in 95% ethanol. The sample was diluted to about 50ml and allowed to stand approximately 90 minutes. The precipitate was filtered off, dried and weighed.

1. Palladous Sulfate (Tetraaquopalladium (II)) Solution

The arithmetic mean of the Pd (II) content of the tetraaquo-palladium (II) stock was 0.0230 g/sample with an average deviation of 0.0003, which is considered good precision. The calculated molarity was 0.0227M.

2. Sodium Tetrachloropalladate Solution

The tetrachloropalladate stock was analyzed to have 0.1266 ± 0.0002 g/sample Pd (II) or a calculated molarity of 0.0940M.

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C. EQUIPMENT

Spectral scans were taken on a Beckman model DK-1A recording spectrophotometer utilizing one-cm silica cells. Both the reference and the sample cell compartments were thermostated at 25°C by means of circulating water from a temperature controlled water bath. Temperatures rarely fluctuated more than ± 0.1°C.

D. ABSORBANCE RUNS

To insure uniformity in procedures, all solutions sat for a minimum of 24 hours before spectral scans were taken even though previous experiments on rates of anation of Pd(II), using both stopped flow methods and hand injection methods with the DK-1A indicate that the rate of the chloride-ion complexing with palladium (II) is rapid enough that thermodynamic stability was reached long before that time. During scanning, the reference and sample solutions were identical except that the reference solution contained no palladium (II). The DK-1A was recalibrated at both zero percent transmittance and 100 percent transmittance prior to running the spectral scan for each sample solution. Data obtained from the scans of the solutions prepared from the tetraaquopalladium (II) stock are contained in Appendix B, and Fig. (1) is a composite of the absorbance scans. Appendix C and Fig. (2) are analogous for solutions prepared from the tetrachloropalladate stock. Specifically, the spectra in figures (1) and (2) are a measure of absorbance vs. Cl⁻ concentration.

TABLE I

SOLUTIONS PREPARED FROM TETRAAQUOPALLADIUM (II) STOCK

The following solutions were all 100ml solutions using the tetra-aquopalladium (II) stock as solvent. Molarities were calculated to three significant figures.

Solution Number	NaCl Added (grams)	Conc Pd (M)	Conc Cl$^-$ (M)
1	0.1169	0.0227	0.02000
2	0.0234	0.0227	0.00400
3	0.0117	0.0227	0.00200
4	0.0058	0.0227	0.00100
5	0.0012	0.0227	0.00020
6	0.0	0.0227	0.0

FIGURE (1)

The absorbance curves below are for the solutions listed in Table I.
As Cl⁻ concentration decreased, the absorbance decreased and the maximum
absorbance peak moved to lower wavelengths.
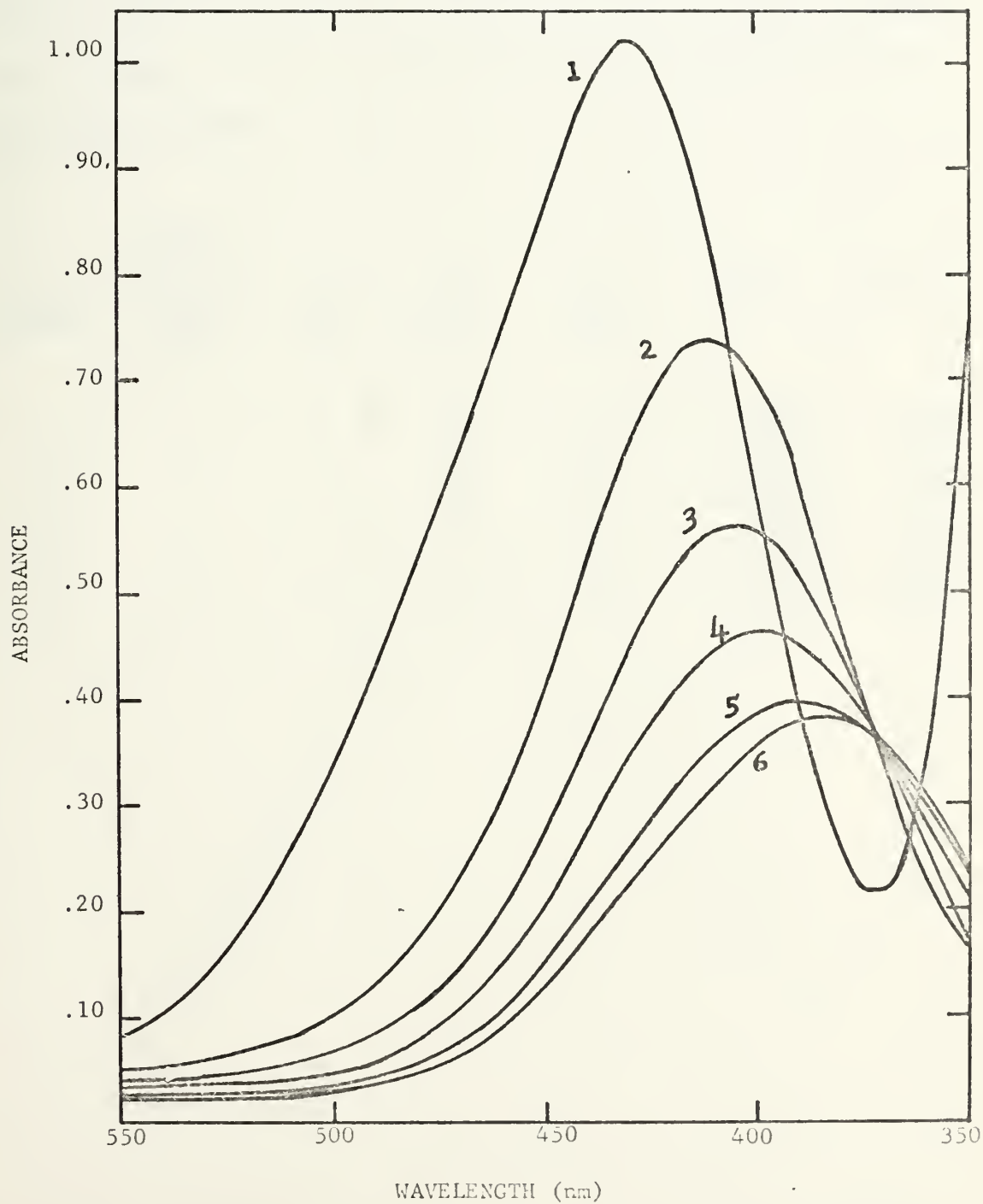
TABLE II

SOLUTIONS PREPARED FROM TETRACHLOROPALLADATE STOCK

The following solutions were prepared volumetrically by adding listed amounts of the tetrachloropalladate stock, 2.0M NaCl, 1.0M HCl, and 1.0M $HClO_4$. Pd and Cl^- concentrations were calculated to three significant figures.

Solution Number	Tetra-chloro-palladate Stock (ml)	2.0M NaCl (ml)	1.0M HCl (ml)	1.0M $HClO_4$ (ml)	Conc Pd	Conc Cl^-
1	3	3	94	0	0.00282	1.0030
2	3	3	53	41	0.00282	0.5930
3	3	3	34	60	0.00282	0.4030
4	3	3	24	70	0.00282	0.3030
5	3	3	4	90	0.00282	0.1030
6	3	0	6	91	0.00282	0.0630
7	3	0	3	94	0.00282	0.0330
8	3	0	1	96	0.00282	0.0130

FIGURE (2)

The absorbance curves below are for solutions listed in Table II. As Cl^- concentration decreased, the absorbance increased and the maximum absorbance peak moved to lower wavelengths.
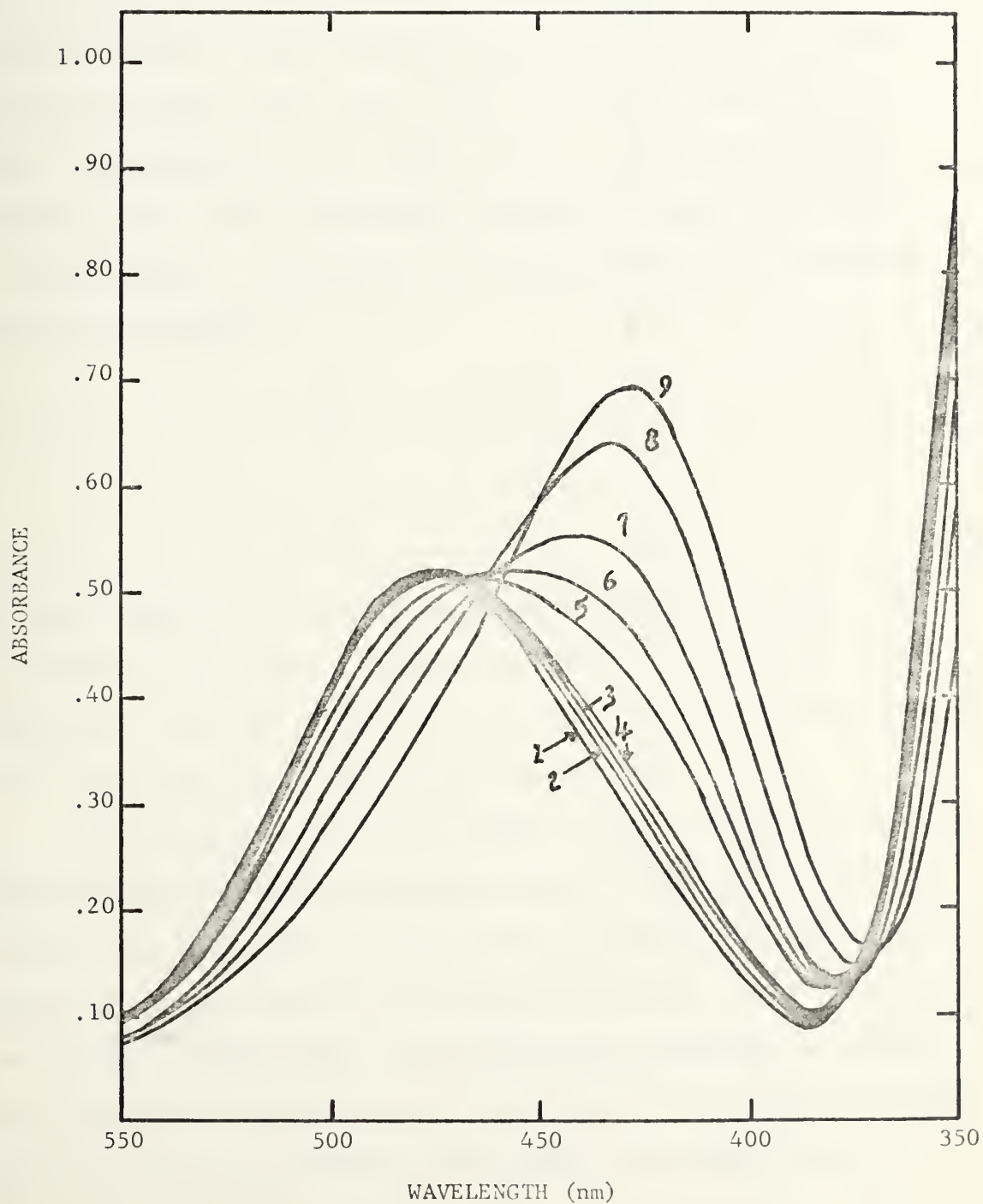
III. TREATMENT OF DATA AND RESULTS

A. DETERMINATION OF STABILITY CONSTANTS

1. General

To determine the stability constants of the Cl^- complexes of Pd(II), a method of curve fitting developed by Srivastava and Newman [Ref. 19] in their study of Br^- and Cl^- complexes of Pd(II) was utilized. In the general case, where X and Y are monodentate ligands and M is a metal which forms square-planar complexes, the formation of mixed complexes of the system may be represented by the following replacement reactions:

$$MX_4 + Y \overset{\beta_1}{\rightleftharpoons} MX_3Y + X \tag{1}$$

$$MX_4 + 2Y \overset{\beta_2}{\rightleftharpoons} MX_2Y_2 + 2X \tag{2}$$

$$MX_4 + 3Y \overset{\beta_3}{\rightleftharpoons} MXY_3 + 3X \tag{3}$$

$$MX_4 + 4Y \overset{\beta_4}{\rightleftharpoons} MY_4 + 4X \tag{4}$$
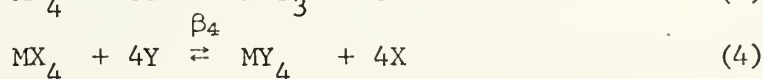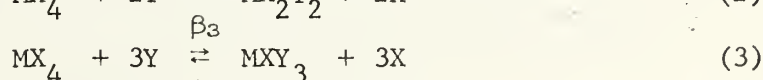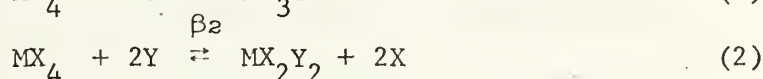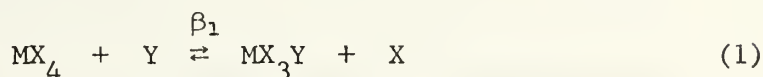
In the situation where X and Y are the only complexing ligands, the equilibria of the entire system can be catagorized by starting with either MX_4 or MY_4 and looking at the replacement of two ligands. Therefore, only reactions (1) and (2) need be studied.

The isosbestic point ($\lambda = 372$nm) in Fig. (1) indicated that no more than two absorbing species were present in the solutions being scanned [Ref. 20]. These species would be $Pd(OH_2)_4^{2+}$ and $Pd(OH_2)_3Cl^+$. Similarly for the other end of the system (Fig. (2)) the species present were $PdCl_4^{2-}$ and $PdCl_3(OH_2)^-$. By sufficiently increasing the ligand ratio, R, the absorbance spectrum moved away from the isosbestic point which indicated the formation of $PdCl_2(OH_2)_2$ for either case. The

ligand ratio was defined as the ratio of Y to X, such that when starting with $Pd(OH_2)_4^{2+}$, $R = [Cl^-]$, and when starting with $PdCl_4^{2-}$, $R = 1/[Cl^-]$.

2. First Step Constants

When just two absorbing species are in equilibrium with each-other, then from Beer's Law and the additive property of absorbances, the total absorbance of the two species can be shown [Ref. 19] to be

$$A = \frac{A_o + A_1\beta_1 R}{1 + \beta_1 R}$$

where, A = measured absorbance of the equilibrium mixture,
A_o = absorbance of the parent complex (MX_4 or MY_4) provided all Pd were of that form,
A_1 = absorbance of the second complex (MX_3Y or MY_3X) provided all Pd were of that form,
β_1 = formation constant, reaction (1),
and R = ligand ratio.

By defining a term, $\Delta = A_o - A_1$, and algebraically manipulating the absorbance equation above, the following expression was obtained:

$$\Delta(1 + \beta_1 R)^{-1} = A - A_1.$$

A second variable was defined as $V = 1 + \beta_1 R$, so that upon substitution into the preceding equation, the following were found:

$$\Delta V^{-1} = A - A_1$$

and
$$\log (V-1) = \log R + \log \beta_1.$$

A set of normalized curves, ΔV^{-1} vs. $\log (V-1)$ was calculated (Appendix A) by assuming various values for Δ and V. The values were plotted in Fig. (3). Plots of A vs. log R from Appendices B and C were then constructed and superimposed on that normalized curve which gave the best fit. Log β_1 was obtained from the translation in the abscissa and A_1 from the translation in the ordinate. The values obtained from the plots at various wavelengths were in close agreement. Each value obtained was weighted equally and a simple average taken to obtain the

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FIGURE (3)

The curves below are plotted from the data in Appendix A. The data from appendices B and C were fitted to these curves to determine values for A_1 and $\log \beta_1$.
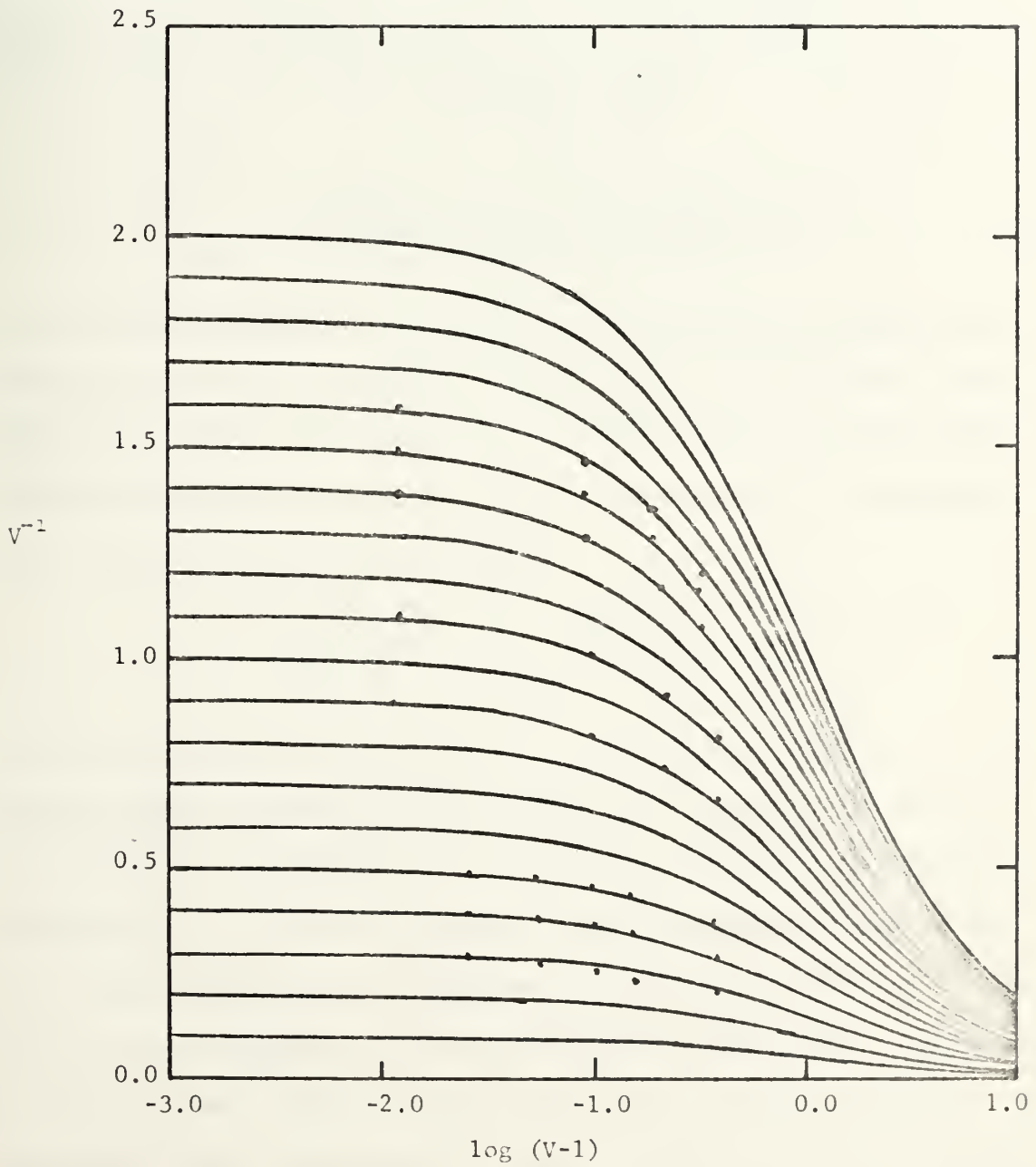
reported value. The two first step values obtained were

$$\log \beta_1 = \log K_1 = [PdCl(OH_2)_3^+]/[Pd(OH_2)_4^{2+}][Cl^-] = 1.887 \pm 0.028, \text{ and}$$

$$\log \beta_1' = \log K_4 = [PdCl_4^{2-}]/[PdCl_3(OH_2)^-][Cl^-] = 1.441 \pm 0.054.$$

3. Second Step Constants

As shown previously, when R was changed sufficiently, a third

complex, $PdCl_2(OH_2)_2$, was formed and was in equilibrium with the other

two complexes. Due to the presence of this new complex, more terms

appear in the expression for the absorbance as follows:

$$A = \frac{A_o + A_1\beta_1 R + A_2\beta_2 R^2}{1 + \beta_1 R + \beta_2 R^2}$$

where, A_2 = absorbance of the third complex (MX_2Y_2)
provided all Pd were of that form,
and β_2 = formation constant, reaction (2).

Of the methods available to solve for the individual absorbances and

formation constants, including solution of sets of simultaneous equa-

tions, the method that allowed for the easiest handling of absorbance

data was to manipulate the equation into the equation of a straight

line. The equation [Ref. 19] became

$$\frac{(A - A_2)R^2}{(A_o - A)} = 1/\beta_2 + \frac{R(A_1 - A)}{(A_o - A)} \beta_1/\beta_2 .$$

The values of A_2 were assumed and the left hand term calculated using a

Hewlett-Packard Calculator Model 9100A. The values for the left hand

term and values calculated for $R(A_1 - A)/(A_o - A)$ using the previously

determined A_1 were then entered into a linear regression program [Ref.

21]. The output from the program was a correlation coefficient, r, and

the slope and intercept of the corresponding straight line. The values

yielding the best correlation were used and β_2 was calculated from the

intercept value. A check was also made on previously calculated values

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of β_1 by using the slope and the value just obtained for β_2. The values obtained for log K_1 by the two methods agreed within 4% and for log K_4 within 6%.

The method of mathematical handling of the data for the determination of the second step stability constants dictated a statistical adjustment of the values calculated. Naturally the data with the better correlation coefficient should be weighted more heavily than those not having good correlation. Therefore, the data were weighted statistically as follows:

$$\log \beta_2 = \frac{\sum_i (1/(1 - r_i^2))(\log \beta_{2i})}{\sum_i 1/(1 - r_i^2)}$$

where, r_i = correlation coefficient,
and $\log \beta_{2i}$ = value of log β_2 corresponding to data yielding correlation coefficient r_i.

The stepwise formation constants were then calculated from log β_2 using the equation

$$\log K_2 = \log \beta_2 - \log K_1.$$

Values obtained for the second step formation constants were

$\log K_2 = [PdCl_2(OH_2)_2]/[PdCl(OH_2)_3^+][Cl^-]$ = 2.070 ± 0.028 and

$\log K_3 = [PdCl_3(OH_2)^-]/[PdCl_2(OH_2)_2][Cl^-]$ = 2.417 ± 0.054.

B. ABSORBANCES AND INDIVIDUAL CONSTANTS

The absorbances obtained as a function of wavelength and the individual stability constants calculated at various wavelengths are tabulated in Appendix D.

IV. DISCUSSION

A. ESTIMATED STATISTICAL VALUES

Values of K_i, as i increases, are expected to decrease steadily
provided there are only slight changes in the metal-ligand bond energies
[Ref. 1]. This expectation is based on several factors including
steric hindrance, coulombic factors, and statistical factors. Steric
hindrance should not have had a great impact on the values obtained
for the system studied in this research because even though the Cl^-
is a large ion, it does not have the bulk of the H_2O molecule it re-
placed. Coulombic factors would definitely cause a decrease in pro-
gressive values of the K_i's in this system because as each successive
Cl^- is bonded to the Pd(II), the charge on the complex would become less
attractive to another Cl^-. Statistical factors are somewhat more in-
volved than the qualitative discussions rendered steric hindrance and
coulombic factors. In the case studied, the coordination number of
the Pd(II) was four and remained so throughout the successive replacement
reactions. When the coordination number remains the same, the series
can be represented, in the general form, as $M(OH_2)_N$ . . . $M(OH_2)_{N-n}X_n$ . . .
MX_n. The $M(OH_2)_{N-n}X_n$ species has n locations from which to lose a
ligand, whereas the next species in the series, $M(OH_2)_{N-n+1}X_{n+1}$, would
have N-n+1 sites at which to gain a ligand. Therefore, the probability
of the ligand replacement taking place is proportional to (N-n+1)/n.
Similarly, the probability of the next replacement taking place is
proportional to (N-n)/(n+1). Therefore, on statistical considerations
alone, a ratio of statistical constants can be shown to be:

$$\frac{K_{n+1}}{K_n} = \frac{n(N-n)}{(n+1)(N-n+1)} \qquad \text{[Ref. 1].}$$

The values tabulated below are comparisons of the estimated statistical values and the experimental values from this work.

	Statistical	Experimental
K_2/K_1	0.375	1.52
K_3/K_2	0.444	1.85
K_4/K_3	0.375	0.106

B. COMPARISONS

The tremendous deviations in statistical and experimental values, in the first two cases, led to other investigations which revealed even more anomalies. The value for K_1 became suspect when it was discovered that even though the absorbance curve for the starting material fit the general shape and λ_{max} of a $Pd(OH_2)_4^{2+}$ spectrum [Refs. 11,16], ϵ for the species at A_{max} = 384nm was only 19 as compared to the generally accepted value of 80 [Ref. 11]. Additionally, the value found for K_1 was extremely low compared to the values reported by Shchukarev et al [Ref. 14], Burger [Ref. 13], Weed [Ref. 12], and Droll [Ref. 10].

The value reported by Droll is, however, considered high in light of work reported by Rasmussen and Jørgensen [Ref. 11], which included a study of the replacement of Pd(II) by Hg(II) to form $HgCl_4^{2-}$. Since the replacement goes almost to completion, and the values of log K_1 and log K_2 for Hg(II) chloro complexes are 6.74 and 6.48, then log K_1 for the Pd(II) system must be less than 6. It is also suspected that Droll might have had the wrong starting material, since it was prepared from PdO. Rasmussen and Jørgensen have determined that solutions prepared thus from PdO in $HClO_4$ have higher extinction and develop a dark decomposition product that precipitates out with time.

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Early work in this research included a method of estimating the location of absorption maxima of the various chloro complexes of Pd(II). The method employed was to plot wavelength $\underline{vs}$ wave number and assume an equidistant relationship between A_{max} peaks for the species with respect to wave number. The wave number values obtained were then converted to wavelength via the plot. The estimated locations and the experimentally determined locations are listed below.

	Estimated	Experimental
$PdCl_4^{2-}$	475nm	475nm
$PdCl_3(OH_2)^-$	447nm	430nm
$PdCl_2(OH_2)_2$	423nm	430nm, 455nm
$PdCl(OH_2)_3^+$	401nm	420nm
$Pd(OH_2)_4^{2+}$	381nm	384nm

Two values for the location of A_{max} for the $PdCl_2(OH_2)_2$ species were calculated since it was approached from both ends of the system. Two anomalies exist in the values -- first, they do not agree with each other, and second, one of the values would have the A_{max} located between the absorbance maxima of $PdCl_4^{2-}$ and $PdCl_3(OH_2)^-$ which is most unlikely. A final irregularity was that the value for K_2 was also very low as compared to values of the same workers cited before (Shchukarev, Burger, Weed, and Droll). This anomaly can be explained on the basis that the values of A_1 which were obtained using the suspect $Pd(OH_2)_4^{2+}$ starting material were used in the calculations of β_2, thereby compounding the error. The values on the other end of the system appear to be quite satisfactory in comparison to the values of the other workers and in comparison to the statistically predicted values. Additionally, the ϵ_{max} for the $PdCl_4^{2-}$ starting material was 173 which compares favorably with the 159 value reported by Cohen and Davidson [Ref. 17]. The

location of A_{max} for the $PdCl_3(OH_2)^-$ species did not appear at the wavelength predicted by the wavelength vs. wave number plot, but that prediction was only a first approximation.

C. CONCLUSION

Little can be discussed about the values reported by Burger and by Weed because their papers were not available. Shchukarev's report appears to give few details about experimental procedure. A value for K_4 was reported by Schwab and Rund [Ref. 22], reported as the equilibrium of the tetrachloro species with the solvated species, the equilibrium being a part of a proposed kinetic mechanism for the replacement of two chloride ions by the bidentate ligand, 2,2' - Bipyridyl. This was calculated, along with two rate constants, by solving sets of simultaneous rate equations utilizing k_{obsd} values for the above mentioned bipy replacement. The value reported was 3.2×10^{-3} or $\log K_4 = 2.5$, which is, like Droll's, high compared to the other values for K_4.

Values of K_4 and K_3 obtained from this research appear to be reliable based on comparisons with values of other workers, the agreement among the various values obtained from each data set, and the comparison to the statistical estimations.

On the other hand, further work is definitely needed in the determination of values for K_2 and K_1. As pointed out there is a great deal of doubt as to the reliability of these two values as well as the locations of A_{max} for the middle three species of the series. The values are suspect based primarily on the fact that possibly the starting material was not $Pd(OH_2)_4^{2+}$. It is considered that the method of preparation of $Pd(OH_2)_4^{2+}$ (boiling $Pd(NO_3)_2$ in concentrated H_2SO_4) is the most convenient. It should also be pointed out that since NO_3^- is a

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good absorber in this spectral region, if any NO_3^- happened to not be driven off in the boiling process, the resulting solution of $PdSO_4$ in $HClO_4$ would yield a larger ϵ_{max} than the ϵ_{max} obtained in this work. Additional information of interest would be to calculate the ϵ's for all of the species, once all of the K_i's and A_i's had been obtained and checked. The method of calculation would be Beer's Law as it is written in the introduction of this report. The advantage of calculating the ϵ's would be the ability to reconstruct the absorbance curves of the various individual species of the system. The method of checking the values obtained for K_1 through K_4 and A_o through A_4 would be to substitute corresponding values for β_1 through β_4 and A_o through A_4 into the absorbance equation described in the treatment of data and results section and reconstruct the curves in Figs. (1) and (2).

APPENDIX A

NORMALIZED CURVES DATA

This Appendix contains all calculated data used in plotting the normalized curves of Fig. (3). Curves for $\Delta = 0.1$ and $\Delta = -0.1$ are mirror images of each other across the horizontal (log (V-1)) axis.

$$\Delta = 0.1$$

V	V^{-1}	ΔV^{-1}	V-1	log (V-1)
1.01	0.9901	0.099	0.01	-2.000
1.02	0.9804	0.098	0.02	-1.699
1.03	0.9709	0.097	0.03	-1.523
1.04	0.9615	0.096	0.04	-1.398
1.05	0.9524	0.095	0.05	-1.301
1.06	0.9434	0.094	0.06	-1.222
1.07	0.9346	0.094	0.07	-1.155
1.08	0.9259	0.093	0.08	-1.097
1.09	0.9174	0.092	0.09	-1.046
1.10	0.9091	0.091	0.10	-1.000
1.12	0.8929	0.089	0.12	-0.921
1.15	0.8696	0.087	0.15	-0.824
1.20	0.8333	0.083	0.20	-0.699
1.25	0.8000	0.080	0.25	-0.602
1.32	0.7576	0.076	0.32	-0.495
1.40	0.7143	0.071	0.40	-0.398
1.50	0.6667	0.067	0.50	-0.301
1.63	0.6135	0.061	0.63	-0.201
1.79	0.5587	0.056	0.79	-0.102
2.00	0.5000	0.050	1.00	0.000
3.00	0.3333	0.033	2.00	0.301
4.00	0.2500	0.025	3.00	0.477
5.00	0.2000	0.020	4.00	0.602
6.00	0.1667	0.017	5.00	0.669
7.00	0.1433	0.014	6.00	0.778
8.00	0.1250	0.013	7.00	0.845
9.00	0.1111	0.011	8.00	0.903
10.00	0.1000	0.010	9.00	0.954

$$\triangle = 0.2$$

V	V^{-1}	$\triangle V^{-1}$	V-1	log (V-1)
1.01	0.9901	0.198	0.01	-2.000
1.02	0.9804	0.196	0.02	-1.699
1.03	0.9709	0.194	0.03	-1.523
1.04	0.9615	0.192	0.04	-1.398
1.05	0.9524	0.191	0.05	-1.301
1.06	0.9434	0.189	0.06	-1.222
1.07	0.9346	0.187	0.07	-1.155
1.08	0.9259	0.185	0.08	-1.097
1.09	0.9174	0.184	0.09	-1.046
1.10	0.9091	0.182	0.10	-1.000
1.12	0.8929	0.179	0.12	-0.921
1.15	0.8696	0.174	0.15	-0.824
1.20	0.8333	0.167	0.20	-0.699
1.25	0.8000	0.160	0.25	-0.602
1.32	0.7576	0.152	0.32	-0.495
1.40	0.7143	0.143	0.40	-0.398
1.50	0.6667	0.133	0.50	-0.301
1.63	0.6135	0.123	0.63	-0.201
1.79	0.5587	0.112	0.79	-0.102
2.00	0.5000	0.100	1.00	0.000
3.00	0.3333	0.067	2.00	0.301
4.00	0.2500	0.050	3.00	0.477
5.00	0.2000	0.040	4.00	0.602
6.00	0.1667	0.033	5.00	0.699
7.00	0.1433	0.029	6.00	0.778
8.00	0.1250	0.025	7.00	0.845
9.00	0.1111	0.022	8.00	0.903
10.00	0.1000	0.020	9.00	0.954

$$\triangle = 0.3$$

V	V^{-1}	$\triangle V^{-1}$	V-1	log (V-1)
1.01	0.9901	0.297	0.01	-2.000
1.02	0.9804	0.294	0.02	-1.699
1.03	0.9709	0.291	0.03	-1.523
1.04	0.9615	0.289	0.04	-1.398
1.05	0.9524	0.286	0.05	-1.301
1.06	0.9434	0.283	0.06	-1.222
1.07	0.9346	0.284	0.07	-1.155
1.08	0.9259	0.278	0.08	-1.097
1.09	0.9174	0.275	0.09	-1.046
1.10	0.9091	0.273	0.10	-1.000
1.12	0.8929	0.268	0.12	-0.921
1.15	0.8696	0.261	0.15	-0.824
1.20	0.8333	0.250	0.20	-0.699
1.25	0.8000	0.240	0.25	-0.602
1.32	0.7576	0.228	0.32	-0.495
1.40	0.7143	0.214	0.40	-0.398
1.50	0.6667	0.200	0.50	-0.301
1.63	0.6135	0.184	0.63	-0.201
1.79	0.5587	0.167	0.79	-0.102
2.00	0.5000	0.150	1.00	0.000
3.00	0.3333	0.100	2.00	0.301
4.00	0.2500	0.075	3.00	0.477
5.00	0.2000	0.060	4.00	0.602
6.00	0.1667	0.050	5.00	0.699
7.00	0.1433	0.043	6.00	0.778
8.00	0.1250	0.038	7.00	0.845
9.00	0.1111	0.033	8.00	0.903
10.00	0.1000	0.030	9.00	0.954

$$\triangle = 0.4$$

V	V^{-1}	$\triangle V^{-1}$	V-1	log (V-1)
1.01	0.9901	0.396	0.01	-2.000
1.02	0.9804	0.392	0.02	-1.699
1.03	0.9709	0.388	0.03	-1.523
1.04	0.9615	0.385	0.04	-1.398
1.05	0.9524	0.381	0.05	-1.301
1.06	0.9434	0.377	0.06	-1.222
1.07	0.9346	0.374	0.07	-1.155
1.08	0.9259	0.370	0.08	-1.097
1.09	0.9174	0.367	0.09	-1.046
1.10	0.9091	0.364	0.10	-1.000
1.12	0.8929	0.357	0.12	-0.921
1.15	0.8696	0.348	0.15	-0.824
1.20	0.8333	0.333	0.20	-0.699
1.25	0.8000	0.320	0.25	-0.602
1.32	0.7576	0.303	0.32	-0.495
1.40	0.7143	0.286	0.40	-0.398
1.50	0.6667	0.267	0.50	-0.301
1.63	0.6135	0.245	0.63	-0.201
1.79	0.5587	0.224	0.79	-0.102
2.00	0.5000	0.200	1.00	0.000
3.00	0.3333	0.133	2.00	0.301
4.00	0.2500	0.100	3.00	0.477
5.00	0.2000	0.080	4.00	0.602
6.00	0.1667	0.067	5.00	0.699
7.00	0.1433	0.057	6.00	0.778
8.00	0.1250	0.050	7.00	0.845
9.00	0.1111	0.044	8.00	0.903
10.00	0.1000	0.040	9.00	0.954

$$\triangle = 0.5$$

V	V^{-1}	$\triangle V^{-1}$	V-1	log (V-1)
1.01	0.9901	0.495	0.01	-2.000
1.02	0.9804	0.490	0.02	-1.699
1.03	0.9709	0.485	0.03	-1.523
1.04	0.9615	0.481	0.04	-1.398
1.05	0.9524	0.476	0.05	-1.301
1.06	0.9434	0.472	0.06	-1.222
1.07	0.9346	0.467	0.07	-1.155
1.08	0.9259	0.463	0.08	-1.097
1.09	0.9174	0.459	0.09	-1.046
1.10	0.9091	0.455	0.10	-1.000
1.12	0.8929	0.447	0.12	-0.921
1.15	0.8696	0.435	0.15	-0.824
1.20	0.8333	0.417	0.20	-0.699
1.25	0.8000	0.400	0.25	-0.602
1.32	0.7576	0.379	0.32	-0.495
1.40	0.7143	0.357	0.40	-0.398
1.50	0.6667	0.333	0.50	-0.301
1.63	0.6135	0.307	0.63	-0.201
1.79	0.5587	0.279	0.79	-0.102
2.00	0.5000	0.250	1.00	0.000
3.00	0.3333	0.167	2.00	0.301
4.00	0.2500	0.125	3.00	0.477
5.00	0.2000	0.100	4.00	0.602
6.00	0.1667	0.084	5.00	0.699
7.00	0.1433	0.072	6.00	0.778
8.00	0.1250	0.063	7.00	0.845
9.00	0.1111	0.056	8.00	0.903
10.00	0.1000	0.050	9.00	0.954

$$\triangle = 0.6$$

V	V^{-1}	$\triangle$V^{-1}	V-1	log (V-1)
1.01	0.9901	0.594	0.01	-2.000
1.02	0.9804	0.588	0.02	-1.699
1.03	0.9709	0.583	0.03	-1.523
1.04	0.9615	0.577	0.04	-1.398
1.05	0.9524	0.572	0.05	-1.301
1.06	0.9434	0.566	0.06	-1.222
1.07	0.9346	0.561	0.07	-1.155
1.08	0.9259	0.556	0.08	-1.097
1.09	0.9174	0.550	0.09	-1.046
1.10	0.9091	0.546	0.10	-1.000
1.12	0.8929	0.536	0.12	-0.921
1.15	0.8696	0.522	0.15	-0.824
1.20	0.8333	0.500	0.20	-0.699
1.25	0.8000	0.480	0.25	-0.602
1.32	0.7576	0.455	0.32	-0.495
1.40	0.7143	0.429	0.40	-0.398
1.50	0.6667	0.400	0.50	-0.301
1.63	0.6135	0.368	0.63	-0.201
1.79	0.5587	0.335	0.79	-0.102
2.00	0.5000	0.300	1.00	0.000
3.00	0.3333	0.200	2.00	0.301
4.00	0.2500	0.150	3.00	0.477
5.00	0.2000	0.120	4.00	0.602
6.00	0.1667	0.100	5.00	0.699
7.00	0.1433	0.086	6.00	0.778
8.00	0.1250	0.075	7.00	0.845
9.00	0.1111	0.067	8.00	0.903
10.00	0.1000	0.060	9.00	0.954

$$\triangle = 0.7$$

V	V^{-1}	$\triangle V^{-1}$	V-1	log (V-1)
1.01	0.9901	0.693	0.01	-2.000
1.02	0.9804	0.686	0.02	-1.699
1.03	0.9709	0.680	0.03	-1.533
1.04	0.9615	0.673	0.04	-1.398
1.05	0.9524	0.667	0.05	-1.301
1.06	0.9434	0.660	0.06	-1.222
1.07	0.9346	0.654	0.07	-1.155
1.08	0.9259	0.648	0.08	-1.097
1.09	0.9174	0.642	0.09	-1.046
1.10	0.9091	0.636	0.10	-1.000
1.12	0.8929	0.625	0.12	-0.921
1.15	0.8696	0.609	0.15	-0.824
1.20	0.8333	0.583	0.20	-0.699
1.25	0.8000	0.560	0.25	-0.602
1.32	0.7576	0.530	0.32	-0.495
1.40	0.7143	0.500	0.40	-0.398
1.50	0.6667	0.467	0.50	-0.301
1.63	0.6135	0.430	0.63	-0.201
1.79	0.5587	0.391	0.79	-0.102
2.00	0.5000	0.350	1.00	0.000
3.00	0.3333	0.233	2.00	0.301
4.00	0.2500	0.175	3.00	0.477
5.00	0.2000	0.140	4.00	0.602
6.00	0.1667	0.117	5.00	0.699
7.00	0.1433	0.100	6.00	0.778
8.00	0.1250	0.088	7.00	0.845
9.00	0.1111	0.078	8.00	0.903
10.00	0.1000	0.070	9.00	0.954

$$\Delta = 0.8$$

V	V^{-1}	ΔV^{-1}	V-1	log (V-1)
1.01	0.9901	0.792	0.01	-2.000
1.02	0.9804	0.784	0.02	-1.699
1.03	0.9709	0.777	0.03	-1.523
1.04	0.9615	0.769	0.04	-1.398
1.05	0.9524	0.762	0.05	-1.301
1.06	0.9434	0.755	0.06	-1.222
1.07	0.9346	0.748	0.07	-1.155
1.08	0.9259	0.741	0.08	-1.097
1.09	0.9174	0.734	0.09	-1.046
1.10	0.9091	0.727	0.10	-1.000
1.12	0.8929	0.714	0.12	-0.921
1.15	0.8696	0.696	0.15	-0.824
1.20	0.8333	0.667	0.20	-0.699
1.25	0.8000	0.640	0.25	-0.602
1.32	0.7576	0.606	0.32	-0.495
1.40	0.7143	0.571	0.40	-0.398
1.50	0.6667	0.533	0.50	-0.301
1.63	0.6135	0.491	0.63	-0.201
1.79	0.5587	0.447	0.79	-0.102
2.00	0.5000	0.400	1.00	0.000
3.00	0.3333	0.266	2.00	0.301
4.00	0.2500	0.200	3.00	0.477
5.00	0.2000	0.160	4.00	0.602
6.00	0.1667	0.134	5.00	0.699
7.00	0.1433	0.114	6.00	0.778
8.00	0.1250	0.100	7.00	0.845
9.00	0.1111	0.089	8.00	0.903
10.00	0.1000	0.080	9.00	0.954

$$\Delta = 0.9$$

V	V^{-1}	ΔV^{-1}	V-1	log (V-1)
1.01	0.9901	0.891	0.01	-2.000
1.02	0.9804	0.882	0.02	-1.699
1.03	0.9709	0.874	0.03	-1.523
1.04	0.9615	0.865	0.04	-1.398
1.05	0.9524	0.857	0.05	-1.301
1.06	0.9434	0.849	0.06	-1.222
1.07	0.9346	0.841	0.07	-1.155
1.08	0.9259	0.833	0.08	-1.097
1.09	0.9174	0.826	0.09	-1.046
1.10	0.9091	0.818	0.10	-1.000
1.12	0.8929	0.804	0.12	-0.921
1.15	0.8696	0.783	0.15	-0.824
1.20	0.8333	0.750	0.20	-0.699
1.25	0.8000	0.720	0.25	-0.602
1.32	0.7576	0.682	0.32	-0.495
1.40	0.7143	0.643	0.40	-0.398
1.50	0.6667	0.600	0.50	-0.301
1.63	0.6135	0.552	0.63	-0.201
1.79	0.5587	0.503	0.79	-0.102
2.00	0.5000	0.450	1.00	0.000
3.00	0.3333	0.300	2.00	0.301
4.00	0.2500	0.225	3.00	0.477
5.00	0.2000	0.180	4.00	0.602
6.00	0.1667	0.150	5.00	0.699
7.00	0.1433	0.129	6.00	0.778
8.00	0.1250	0.113	7.00	0.845
9.00	0.1111	0.100	8.00	0.903
10.00	0.1000	0.090	9.00	0.954

$$\Delta = 1.0$$

V	V^{-1}	ΔV^{-1}	V-1	log (V-1)
1.01	0.9901	0.990	0.01	-2.000
1.02	0.9804	0.980	0.02	-1.699
1.03	0.9709	0.971	0.03	-1.523
1.04	0.9615	0.962	0.04	-1.398
1.05	0.9524	0.952	0.05	-1.301
1.06	0.9434	0.943	0.06	-1.222
1.07	0.9346	0.935	0.07	-1.155
1.08	0.9259	0.926	0.08	-1.097
1.09	0.9174	0.917	0.09	-1.046
1.10	0.9091	0.909	0.10	-1.000
1.12	0.8929	0.893	0.12	-0.921
1.15	0.8696	0.870	0.15	-0.824
1.20	0.8333	0.833	0.20	-0.699
1.25	0.8000	0.800	0.25	-0.602
1.32	0.7576	0.758	0.32	-0.495
1.40	0.7143	0.714	0.40	-0.398
1.50	0.6667	0.667	0.50	-0.301
1.63	0.6135	0.614	0.63	-0.201
1.79	0.5587	0.559	0.79	-0.102
2.00	0.5000	0.500	1.00	0.000
3.00	0.3333	0.333	2.00	0.301
4.00	0.2500	0.250	3.00	0.477
5.00	0.2000	0.200	4.00	0.602
6.00	0.1667	0.167	5.00	0.699
7.00	0.1433	0.143	6.00	0.778
8.00	0.1250	0.125	7.00	0.845
9.00	0.1111	0.111	8.00	0.903
10.00	0.1000	0.100	9.00	0.954

$$\triangle = 1.1$$

V	V^{-1}	$\triangle V^{-1}$	V-1	log (V-1)
1.01	0.9901	1.089	0.01	-2.000
1.02	0.9804	1.078	0.02	-1.699
1.03	0.9709	1.068	0.03	-1.523
1.04	0.9615	1.058	0.04	-1.398
1.05	0.9524	1.048	0.05	-1.301
1.06	0.9434	1.038	0.06	-1.222
1.07	0.9346	1.028	0.07	-1.155
1.08	0.9259	1.019	0.08	-1.097
1.09	0.9174	1.009	0.09	-1.046
1.10	0.9091	1.000	0.10	-1.000
1.12	0.8929	0.982	0.12	-0.921
1.15	0.8696	0.957	0.15	-0.824
1.20	0.8333	0.917	0.20	-0.699
1.25	0.8000	0.880	0.25	-0.602
1.32	0.7576	0.833	0.32	-0.495
1.40	0.7143	0.786	0.40	-0.398
1.50	0.6667	0.733	0.50	-0.301
1.63	0.6135	0.675	0.63	-0.201
1.79	0.5587	0.615	0.79	-0.102
2.00	0.5000	0.550	1.00	0.000
3.00	0.3333	0.366	2.00	0.301
4.00	0.2500	0.275	3.00	0.477
5.00	0.2000	0.220	4.00	0.602
6.00	0.1667	0.184	5.00	0.699
7.00	0.1433	0.157	6.00	0.778
8.00	0.1250	0.138	7.00	0.845
9.00	0.1111	0.122	8.00	0.903
10.00	0.1000	0.110	9.00	0.954

$$\triangle = 1.2$$

V	V^{-1}	$\triangle V^{-1}$	V-1	log (V-1)
1.01	0.9901	1.188	0.01	-2.000
1.02	0.9804	1.177	0.02	-1.699
1.03	0.9709	1.165	0.03	-1.523
1.04	0.9615	1.154	0.04	-1.398
1.05	0.9524	1.143	0.05	-1.301
1.06	0.9434	1.132	0.06	-1.222
1.07	0.9346	1.122	0.07	-1.155
1.08	0.9259	1.111	0.08	-1.097
1.09	0.9174	1.101	0.09	-1.046
1.10	0.9091	1.091	0.10	-1.000
1.12	0.8929	1.072	0.12	-0.921
1.15	0.8696	1.044	0.15	-0.824
1.20	0.8333	1.000	0.20	-0.699
1.25	0.8000	0.960	0.25	-0.602
1.32	0.7576	9.909	0.32	-0.495
1.40	0.7143	0.857	0.40	-0.398
1.50	0.6667	0.800	0.50	-0.301
1.63	0.6135	0.736	0.63	-0.201
1.79	0.5587	0.670	0.79	-0.102
2.00	0.5000	0.600	1.00	0.000
3.00	0.3333	0.400	2.00	0.301
4.00	0.2500	0.300	3.00	0.477
5.00	0.2000	0.240	4.00	0.602
6.00	0.1667	0.200	5.00	0.699
7.00	0.1433	0.172	6.00	0.778
8.00	0.1250	0.150	7.00	0.845
9.00	0.1111	0.133	8.00	0.903
10.00	0.1000	0.120	9.00	0.954

$$\triangle = 1.3$$

V	V^{-1}	$\triangle V^{-1}$	V-1	log (V-1)
1.01	0.9901	1.287	0.01	-2.000
1.02	0.9804	1.275	0.02	-1.699
1.03	0.9709	1.262	0.03	-1.523
1.04	0.9615	1.250	0.04	-1.398
1.05	0.9524	1.238	0.05	-1.301
1.06	0.9434	1.226	0.06	-1.222
1.07	0.9346	1.215	0.07	-1.155
1.08	0.9259	1.204	0.08	-1.097
1.09	0.9174	1.193	0.09	-1.046
1.10	0.9091	1.182	0.10	-1.000
1.12	0.8929	1.161	0.12	-0.921
1.15	0.8696	1.131	0.15	-0.824
1.20	0.8333	1.083	0.20	-0.699
1.25	0.8000	1.040	0.25	-0.602
1.32	0.7576	0.985	0.32	-0.495
1.40	0.7143	0.929	0.40	-0.398
1.50	0.6667	0.867	0.50	-0.301
1.63	0.6135	0.798	0.63	-0.201
1.79	0.5587	0.726	0.79	-0.102
2.00	0.5000	0.650	1.00	0.000
3.00	0.3333	0.433	2.00	0.301
4.00	0.2500	0.325	3.00	0.477
5.00	0.2000	0.260	4.00	0.602
6.00	0.1667	0.217	5.00	0.699
7.00	0.1433	0.186	6.00	0.778
8.00	0.1250	0.163	7.00	0.845
9.00	0.1111	0.144	8.00	0.903
10.00	0.1000	0.130	9.00	0.954

$$\triangle = 1.4$$

V·	V^{-1}	$\triangle V^{-1}$	V-1	log (V-1)
1.01	0.9901	1.386	0.01	-2.000
1.02	0.9804	1.373	0.02	-1.699
1.03	0.9709	1.359	0.03	-1.523
1.04	0.9615	1.346	0.04	-1.398
1.05	0.9524	1.333	0.05	-1.301
1.06	0.9434	1.321	0.06	-1.222
1.07	0.9346	1.308	0.07	-1.155
1.08	0.9259	1.296	0.08	-1.097
1.09	0.9174	1.284	0.09	-1.046
1.10	0.9091	1.273	0.10	-1.000
1.12	0.8929	1.250	0.12	-0.921
1.15	0.8696	1.217	0.15	-0.824
1.20	0.8333	1.167	0.20	-0.699
1.25	0.8000	1.120	0.25	-0.602
1.32	0.7576	1.061	0.32	-0.495
1.40	0.7143	1.000	0.40	-0.398
1.50	0.6667	0.933	0.50	-0.301
1.63	0.6135	0.859	0.63	-0.201
1.79	0.5587	0.782	0.79	-0.102
2.00	0.5000	0.700	1.00	0.000
3.00	0.3333	0.466	2.00	0.301
4.00	0.2500	0.350	3.00	0.477
5.00	0.2000	0.280	4.00	0.602
6.00	0.1667	0.234	5.00	0.699
7.00	0.1433	0.200	6.00	0.778
8.00	0.1250	0.175	7.00	0.845
9.00	0.1111	0.155	8.00	0.903
10.00	0.1000	0.140	9.00	0.954

$$\triangle = 1.5$$

V	V^{-1}	$\triangle V^{-1}$	V-1	log (V-1)
1.01	0.9901	1.485	0.01	-2.000
1.02	0.9804	1.471	0.02	-1.699
1.03	0.9709	1.456	0.03	-1.523
1.04	0.9615	1.442	0.04	-1.398
1.05	0.9524	1.429	0.05	-1.301
1.06	0.9434	1.415	0.06	-1.222
1.07	0.9346	1.402	0.07	-1.155
1.08	0.9259	1.389	0.08	-1.097
1.09	0.9174	1.376	0.09	-1.046
1.10	0.9091	1.364	0.10	-1.000
1.12	0.8929	1.339	0.12	-0.921
1.15	0.8696	1.304	0.15	-0.824
1.20	0.8333	1.250	0.20	-0.699
1.25	0.8000	1.200	0.25	-0.602
1.32	0.7576	1.136	0.32	-0.495
1.40	0.7143	1.072	0.40	-0.398
1.50	0.6667	1.000	0.50	-0.301
1.63	0.6135	0.920	0.63	-0.201
1.79	0.5587	0.838	0.79	-0.102
2.00	0.5000	0.750	1.00	0.000
3.00	0.3333	0.500	2.00	0.301
4.00	0.2500	0.375	3.00	0.477
5.00	0.2000	0.300	4.00	0.602
6.00	0.1667	0.251	5.00	0.699
7.00	0.1433	0.215	6.00	0.778
8.00	0.1250	0.188	7.00	0.845
9.00	0.1111	0.167	8.00	0.903
10.00	0.1000	0.150	9.00	0.954

$$\triangle = 1.6$$

V	V^{-1}	$\triangle V^{-1}$	V-1	log (V-1)
1.01	0.9901	1.584	0.01	-2.000
1.02	0.9804	1.569	0.02	-1.699
1.03	0.9709	1.553	0.03	-1.523
1.04	0.9615	1.538	0.04	-1.398
1.05	0.9524	1.524	0.05	-1.301
1.06	0.9434	1.509	0.06	-1.222
1.07	0.9346	1.495	0.07	-1.155
1.08	0.9259	1.481	0.08	-1.097
1.09	0.9174	1.468	0.09	-1.046
1.10	0.9091	1.455	0.10	-1.000
1.12	0.8929	1.429	0.12	-0.921
1.15	0.8696	1.391	0.15	-0.824
1.20	0.8333	1.333	0.20	-0.699
1.25	0.8000	1.280	0.25	-0.602
1.32	0.7576	1.212	0.32	-0.495
1.40	0.7143	1.143	0.40	-0.398
1.50	0.6667	1.067	0.50	-0.301
1.63	0.6135	0.982	0.63	-0.201
1.79	0.5587	0.894	0.79	-0.102
2.00	0.5000	0.800	1.00	0.000
3.00	0.3333	0.533	2.00	0.301
4.00	0.2500	0.400	3.00	0.477
5.00	0.2000	0.320	4.00	0.602
6.00	0.1667	0.267	5.00	0.699
7.00	0.1433	0.229	6.00	0.778
8.00	0.1250	0.200	7.00	0.845
9.00	0.1111	0.178	8.00	0.903
10.00	0.1000	0.160	9.00	0.954

$$\triangle = 1.7$$

V	V^{-1}	$\triangle V^{-1}$	V-1	log (V-1)
1.01	0.9901	1.683	0.01	-2.000
1.02	0.9804	1.667	0.02	-1.699
1.03	0.9709	1.651	0.03	-1.523
1.04	0.9615	1.634	0.04	-1.398
1.05	0.9524	1.619	0.05	-1.301
1.06	0.9434	1.604	0.06	-1.222
1.07	0.9346	1.589	0.07	-1.155
1.08	0.9259	1.574	0.08	-1.097
1.09	0.9174	1.560	0.09	-1.046
1.10	0.9091	1.546	0.10	-1.000
1.12	0.8929	1.518	0.12	-0.921
1.15	0.8696	1.478	0.15	-0.824
1.20	0.8333	1.417	0.20	-0.699
1.25	0.8000	1.360	0.25	-0.602
1.32	0.7576	1.288	0.32	-0.495
1.40	0.7143	1.214	0.40	-0.398
1.50	0.6667	1.133	0.50	-0.301
1.63	0.6135	1.043	0.63	-0.201
1.79	0.5587	0.950	0.79	-0.102
2.00	0.5000	0.850	1.00	0.000
3.00	0.3333	0.566	2.00	0.301
4.00	0.2500	0.425	3.00	0.477
5.00	0.2000	0.340	4.00	0.602
6.00	0.1667	0.284	5.00	0.699
7.00	0.1433	0.243	6.00	0.778
8.00	0.1250	0.213	7.00	0.845
9.00	0.1111	0.189	8.00	0.903
10.00	0.1000	0.170	9.00	0.954

$$\triangle = 1.8$$

V	V^{-1}	$\triangle V^{-1}$	V-1	log (V-1)
1.01	0.9901	1.782	0.01	-2.000
1.02	0.9804	1.765	0.02	-1.699
1.03	0.9709	1.748	0.03	-1.523
1.04	0.9615	1.731	0.04	-1.398
1.05	0.9524	1.714	0.05	-1.301
1.06	0.9434	1.698	0.06	-1.222
1.07	0.9346	1.682	0.07	-1.155
1.08	0.9259	1.667	0.08	-1.097
1.09	0.9174	1.651	0.09	-1.046
1.10	0.9091	1.636	0.10	-1.000
1.12	0.8929	1.607	0.12	-0.921
1.15	0.8696	1.565	0.15	-0.824
1.20	0.8333	1.500	0.20	-0.699
1.25	0.8000	1.440	0.25	-0.602
1.32	0.7576	1.364	0.32	-0.495
1.40	0.7143	1.286	0.40	-0.398
1.50	0.6667	1.200	0.50	-0.301
1.63	0.6135	1.104	0.63	-0.201
1.79	0.5587	1.006	0.79	-0.102
2.00	0.5000	0.900	1.00	0.000
3.00	0.3333	0.599	2.00	0.301
4.00	0.2500	0.450	3.00	0.477
5.00	0.2000	0.360	4.00	0.602
6.00	0.1667	0.301	5.00	0.699
7.00	0.1433	0.257	6.00	0.778
8.00	0.1250	0.225	7.00	0.845
9.00	0.1111	0.200	8.00	0.903
10.00	0.1000	0.180	9.00	0.954

$$\triangle = 1.9$$

V	V^{-1}	$\triangle V^{-1}$	V-1	log (V-1)
1.01	0.9901	1.881	0.01	-2.000
1.02	0.9804	1.863	0.02	-1.699
1.03	0.9709	1.845	0.03	-1.523
1.04	0.9615	1.827	0.04	-1.398
1.05	0.9524	1.810	0.05	-1.301
1.06	0.9434	1.793	0.06	-1.222
1.07	0.9346	1.776	0.07	-1.155
1.08	0.9259	1.759	0.08	-1.097
1.09	0.9174	1.743	0.09	-1.046
1.10	0.9091	1.727	0.10	-1.000
1.12	0.8929	1.697	0.12	-0.921
1.15	0.8696	1.652	0.15	-0.824
1.20	0.8333	1.583	0.20	-0.699
1.25	0.8000	1.520	0.25	-0.602
1.32	0.7576	1.455	0.32	-0.495
1.40	0.7143	1.357	0.40	-0.398
1.50	0.6667	1.267	0.50	-0.301
1.63	0.6135	1.166	0.63	-0.201
1.79	0.5587	1.062	0.79	-0.102
2.00	0.5000	0.950	1.00	0.000
3.00	0.3333	0.633	2.00	0.301
4.00	0.2500	0.475	3.00	0.477
5.00	0.2000	0.380	4.00	0.602
6.00	0.1667	0.317	5.00	0.699
7.00	0.1433	0.272	6.00	0.778
8.00	0.1250	0.238	7.00	0.845
9.00	0.1111	0.211	8.00	0.903
10.00	0.1000	0.190	9.00	0.954

$$\triangle = 2.0$$

V	V^{-1}	$\triangle V^{-1}$	V-1	log (V-1)
1.01	0.9901	1.980	0.01	-2.000
1.02	0.9804	1.961	0.02	-1.699
1.03	0.9709	1.942	0.03	-1.523
1.04	0.9615	1.923	0.04	-1.398
1.05	0.9524	1.905	0.05	-1.301
1.06	0.9434	1.887	0.06	-1.222
1.07	0.9346	1.869	0.07	-1.155
1.08	0.9259	1.852	0.08	-1.097
1.09	0.9174	1.835	0.09	-1.046
1.10	0.9091	1.818	0.10	-1.000
1.12	0.8929	1.786	0.12	-0.921
1.15	0.8696	1.739	0.15	-0.824
1.20	0.8333	1.667	0.20	-0.699
1.25	0.8000	1.600	0.25	-0.602
1.32	0.7576	1.515	0.32	-0.495
1.40	0.7143	1.429	0.40	-0.398
1.50	0.6667	1.333	0.50	-0.301
1.63	0.6135	1.227	0.63	-0.201
1.79	0.5587	1.117	0.79	-0.102
2.00	0.5000	1.000	1.00	0.000
3.00	0.3333	0.666	2.00	0.301
4.00	0.2500	0.500	3.00	0.477
5.00	0.2000	0.400	4.00	0.602
6.00	0.1667	0.334	5.00	0.699
7.00	0.1433	0.286	6.00	0.778
8.00	0.1250	0.250	7.00	0.845
9.00	0.1111	0.222	8.00	0.903
10.00	0.1000	0.200	9.00	0.954

ABSORBANCE DATA FOR DETERMINING K_1 AND K_2

The absorbance data in this appendix came from the spectra of Fig. (1) and was fitted to the normalized curves in Fig (3) to give values of K_1 for the equilibrium:

$$Pd(OH_2)_4^{2+} + Cl^- \overset{K_1}{\rightleftharpoons} PdCl(OH_2)_3^+ + H_2O$$
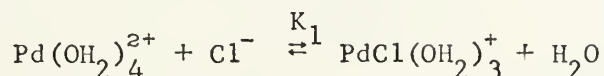
Additionally, the data was used to determine values for K_2 for the equilibrium:

$$PdCl(OH_2)_3^+ + Cl^- \overset{K_2}{\rightleftharpoons} PdCl_2(OH_2)_2 + H_2O$$
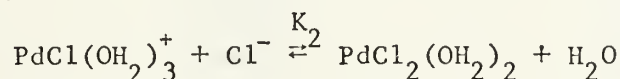
All absorbances were for solutions of unit ionic strength, $[Pd] = 0.0227$, and $T = 25.0^{\circ}C$. Concentrations of Cl^- were accurate to three significant figures and so, therefore, was the ligand ratio, R. Log R is reported to three decimal places. Absorbances are accurate to ± 0.002 absorbance units.

$$\lambda = 390nm$$

Abs.	R	log R
.382	0	$-\infty$
.398	0.00020	-3.699
.452	0.00100	-3.000
.515	0.00200	-2.699
.600	0.00400	-2.398
.400	0.0200	-1.699

$$\lambda = 395nm$$

Abs.	R	log R
.372	0	$-\infty$
.395	0.00020	-3.699
.461	0.00100	-3.000
.540	0.00200	-2.699
.655	0.00400	-2.398
.492	0.0200	-1.699

$$\lambda = 400\text{nm}$$

Abs	R	log R
.361	0	$-\infty$
.387	0.00020	-3.699
.463	0.00100	-3.000
.558	0.00200	-2.699
.700	0.00400	-2.398
.600	0.0200	-1.699

$$\lambda = 405\text{nm}$$

Abs	R	log R
.345	0	$-\infty$
.373	0.00020	-3.699
.460	0.00100	-3.000
.564	0.00200	-2.699
.729	0.00400	-2.398
.694	0.0200	-1.699

$$\lambda = 410\text{nm}$$

Abs	R	log R
.326	0	$-\infty$
.357	0.00020	-3.699
.447	0.00100	-3.000
.560	0.00200	-2.699
.739	0.00400	-2.398
.804	0.0200	-1.699

$$\lambda = 415\text{nm}$$

Abs	R	log R
.305	0	$-\infty$
.336	0.00020	-3.699
.430	0.00100	-3.000
.543	0.00200	-2.699
.738	0.00400	-2.398
.885	0.0200	-1.699

$\lambda = 420$ nm

Abs	R	log R
.284	0	$-\infty$
.315	0.00020	-3.699
.403	0.00100	-3.000
.520	0.00200	-2.699
.717	0.00400	-2.398
.954	0.0200	-1.699

$\lambda = 425$ nm

Abs	R	log R
.256	0	$-\infty$
.289	0.00020	-3.699
.375	0.00100	-3.000
.485	0.00200	-2.699
.682	0.00400	-2.398
.998	0.0200	-1.699

$\lambda = 430$ nm

Abs	R	log R
.235	0	$-\infty$
.262	0.00020	-3.699
.342	0.00100	-3.000
.448	0.00200	-2.699
.636	0.00400	-2.398
1.018	0.0200	-1.699

$\lambda = 435$ nm

Abs	R	log R
.209	0	$-\infty$
.235	0.00020	-3.699
.310	0.00100	-3.000
.401	0.00200	-2.699
.584	0.00400	-2.398
1.010	0.0200	-1.699

$\lambda = 440$ nm

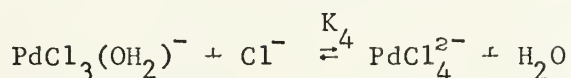| Abs	R	log R
.182	0	$-\infty$
.208	0.00020	-3.699
.265	0.00100	-3.000
.362	0.00200	-2.699
.530	0.00400	-2.398
.978	0.0200	-1.699

ABSORBANCE DATA FOR DETERMINING K_3 AND K_4

The absorbance data in this appendix came from the spectra of

Fig (2) and was used to determine values for K_3 for the equilibrium:

$$PdCl_2(OH_2)_2 + Cl^- \overset{K_3}{\rightleftharpoons} PdCl_3(OH_2)^- + H_2O$$
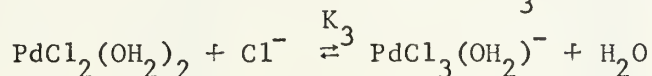
Additionally, the data was fitted to the normalized curves of Fig.

(3) to yield values of K_4 for the reaction:

$$PdCl_3(OH_2)^- + Cl^- \overset{K_4}{\rightleftharpoons} PdCl_4^{2-} + H_2O$$

As in appendix B, the absorbance is accurate to $\pm$ 0.002 absorbance

units and the ligand ratio to three significant figures. Log R is

accurate to three decimal places.

λ = 420 nm

Abs.	R	log R
.240	0.997	-0.001
.257	1.69	0.227
.271	2.48	0.395
.283	3.30	0.519
.368	9.71	0.987
.415	15.9	1.201
.480	30.3	1.481
.587	76.9	1.886
.662	333	2.523

λ = 425 nm

Abs.	R	log R
.270	0.997	-0.001
.285	1.69	0.227
.300	2.48	0.395
.310	3.30	0.519
.400	9.71	0.987
.450	15.9	1.201
.513	30.3	1.481
.618	76.9	1.886
.686	333	2.523

$$\lambda = 430 \text{ nm}$$

Abs.	R	log R
.298	0.997	-0.001
.314	1.69	0.227
.329	2.48	0.395
.341	3.30	0.519
.427	9.71	0.987
.474	15.9	1.201
.538	30.3	1.481
.637	76.9	1.886
.690	333	2.523

$$\lambda = 435 \text{ nm}$$

Abs	R	log R
.332	0.997	-0.001
.343	1.69	0.227
.357	2.48	0.395
.369	3.30	0.519
.448	9.71	0.987
.494	15.9	1.201
.552	30.3	1.481
.639	76.9	1.886
.682	333	2.523

$$\lambda = 440 \text{ nm}$$

Abs	R	log R
.358	0.997	-0.001
.373	1.69	0.227
.385	2.48	0.395
.396	3.30	0.519
.467	9.71	0.987
.506	15.9	1.201
.557	30.3	1.481
.631	76.9	1.886
.658	333	2.523

$$\lambda = 445 \text{ nm}$$

Abs	R	log R
.390	0.997	-0.001
.404	1.69	0.227
.414	2.48	0.395
.420	3.30	0.519
.482	9.71	0.987
.514	15.9	1.201
.555	30.3	1.481
.611	76.9	1.886
.625	333	2.523

$$\lambda = 450 \text{ nm}$$

Abs	R	log R
.422	0.997	-0.001
.433	1.69	0.227
.440	2.48	0.395
.447	3.30	0.519
.493	9.71	0.987
.519	15.9	1.201
.548	30.3	1.481
.586	76.9	1.886
.590	333	2.523

$$\lambda = 455 \text{ nm}$$

Abs	R	log R
.451	0.997	-0.001
.462	1.69	0.227
.466	2.48	0.395
.471	3.30	0.519
.503	9.71	0.987
.522	15.9	1.201
.536	30.3	1.481
.560	76.9	1.886
.545	333	2.523

$$\lambda = 460 \text{ nm}$$

Abs	R	log R
.479	0.997	-0.001
.486	1.69	0.227
.488	2.48	0.395
.490	3.30	0.519
.509	9.71	0.987
.519	15.9	1.201
.521	30.3	1.481
.530	76.9	1.886
.507	333	2.523

$$\lambda = 470 \text{ nm}$$

Abs	R	log R
.515	0.997	-0.001
.518	1.69	0.227
.517	2.48	0.395
.5i5	3.30	0.519
.513	9.71	0.987
.506	15.9	1.201
.487	30.3	1.481
.469	76.9	1.886
.430	333	2.523

$\lambda = 475$ nm

Abs	R	log R
.521	0.997	-0.001
.521	1.69	0.227
.520	2.48	0.395
.517	3.30	0.519
.506	9.71	0.987
.494	15.9	1.201
.465	30.3	1.481
.441	76.9	1.886
.396	333	2.523

$\lambda = 480$ nm

Abs	R	log R
.517	0.997	-0.001
.518	1.69	0.227
.516	2.48	.0.395
.510	3.30	0.519
.493	9.71	0.987
.477	15.9	1.201
.442	30.3	1.481
.410	76.9	1.886
.361	333	2.523

APPENDIX D

ABSORBANCES AND FORMATION CONSTANTS

The data in this appendix are absorbances and overall formation constants determined as a function of wavelength. These data were then used in the calculation of the values reported in this thesis for the four stepwise formation constants of the system going from $Pd(OH_2)_4^{2+}$ to $PdCl_4^{2-}$.

Data for Determining log K_1

λ (nm)	A_1	log β_1
390	1.191	1.960
395	1.580	1.881
400	1.758	1.920
405	1.840	1.905
410	1.928	1.900
415	2.004	1.890
420	2.074	1.884
425	2.048	1.900
430	2.027	1.852
435	1.910	1.835
440	1.774	1.830

Data for Determining log K_2

λ (nm)	A_2	log β_1	log β_2
390	0	2.041	4.009
395	0	1.974	4.000
400	0	1.960	3.896
405	0	1.971	3.813
410	0	1.973	3.705
415	0	1.950	3.600
420	0.077	1.908	3.517
425	0	1.904	3.386
430	0.046	1.851	3.237
435	0.005	1.846	3.097
440	0	1.856	3.062

Data for Determining $\log K_3$

λ (nm)	A'_2	$\log \beta'_1$	$\log \beta'_2$
420	0	1.466	5.312
425	0	1.451	5.238
430	0.026	1.470	4.996
435	0.040	1.351	5.384
440	0.061	1.455	4.870
445	0.080	1.280	5.083
450	0.100	1.263	4.987
455	0.530	1.510	3.225
460	0.485	1.415	3.432
475	0.378	1.714	3.841

Data for Determining $\log K_4$

λ (nm)	A'_1	$\log \beta'_2$
420	0.730	1.450
425	0.758	1.400
430	0.790	1.450
435	0.725	1.400
440	0.760	1.500
445	0.667	1.320
450	0.630	1.380
455	0.650	1.510
460	0.580	1.440
470	0.425	1.560
475	0.420	1.380
480	0.335	1.500

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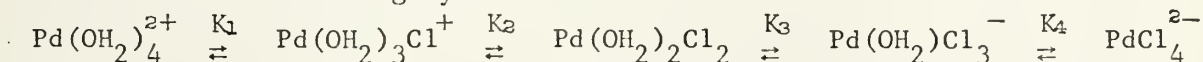
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ABSTRACT

Using absorbance data from Pd (II) solutions containing varying amounts of chloride ion, the stepwise formation constants were determined for the following system:

$$Pd(OH_2)_4^{2+} \;\overset{K_1}{\rightleftarrows}\; Pd(OH_2)_3Cl^+ \;\overset{K_2}{\rightleftarrows}\; Pd(OH_2)_2Cl_2 \;\overset{K_3}{\rightleftarrows}\; Pd(OH_2)Cl_3^- \;\overset{K_4}{\rightleftarrows}\; PdCl_4^{2-}$$

The values for K_1 and K_4 were obtained by curve fitting methods. K_2 and K_3 were found by regression and required statistical adjustment.

Anomalies arising from the resulting values and values obtained by other workers were discussed. Suggestions for further work in the chloro- Pd(II) system were made.

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Stability Constants						
Tetrachloropalladium (II)						
Tetraaquopalladium (II)						

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